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Influences of proton-dissociation equilibrium of capping agents on the photo-chemical events of the colloidal solutions containing the thiol-capped cadmium sulfide particles

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Abstract

The primary photo-chemical events of the aqueous colloidal solutions containing surface-modified CdS particles were investigated by two different methods, of which one employed subpicosecond spectroscopy to measure the transient absorption due to photo-generated electrons in the primary photo-chemical events, and the other stationary irradiation to measure their photo-stability. The pH dependence of transient absorption due to photo-generated electrons (trapped and hydrated electrons) in the colloidal solutions of thioglycerol (TG)-capped CdS (TG-CdS) and mercaptoacetate (MA)-capped CdS (MA-CdS) is similar to that of their photo-stabilities under the stationary irradiation, respectively. However, there was large difference in the pH dependence between TG-CdS and MA-CdS. Namely, the absorption intensity and the photo-stability decrease with lowering pH of the solutions for MA-CdS in the pH range lower than 7, where the negative charge of a carboxyl group of MA is neutralized by addition of proton. However, absorption intensity and photo-stability were hardly influenced by pH of the solution in whole pH range in the case of TG-CdS. These results suggest that the negative charge of the capping agents acts advantageously on the hole-trapping process in the primary photo-chemical events of the surface-modified CdS particles and their photo-stability.

Keywords: Cadmium sulfide; Thioglycerol-capped CdS; Mercaptoacetate-capped CdS; Proton-dissociation equilibrium; Subpicosecond spectroscopy; Photo-stability

1. Introduction

Semiconductor photo-catalytic reactions utilizing intensive redox forces of electrons and holes generated by photo-excitation of semiconductor particles have been studied actively due to their potential attraction for the application to photo-decomposition of water, the removal of environmental pollutants and so on [1–3]. The time-resolved transient absorption spectra of semiconductor particles have also been investigated by a fast kinetic spectroscopy to clarify their primary photo-chemical events [4–22].

In connection with the improvement of the efficiency of the reaction, we have paid attention to the capping agents introduced to the surface of CdS particles to obtain the nanoparticles with a narrow-size distribution, which are convenient for spectroscopic analysis [23–25]. As there is possibility that the capping agents on the surface of the particles act as a relay for the transfer of the photo-generated electrons and holes to reactants locating nearby, it may be meaningful to investigate the role of the capping agent on the primary photo-chemical events of the particles in order to design effective photo-catalysts. For this reason, we have studied the behavior of electrons and holes photo-generated on CdS nanoparticles with the surface modified by capping agents such as thiols, which governs the efficiency of photo-catalytic reactions, from the analysis of their time-resolved transient absorption spectra measured by pump–probe techniques [23–27].

In the present study, as part of our studies for thiol-capped CdS particles, subpicosecond time-resolved transient absorption spectra of mercaptoacetate (MA)-CdS and thioglycerol (TG)-CdS were measured using their aqueous colloidal solutions adjusted at various pH values in order to clarify the influence of the proton-dissociation equilibrium of capping agents on the transfer of the holes photo-generated on the particles to the capping agents. On the other hand, to support the discussion based on pH dependence of the transient absorption, pH dependence of photo-stability of the particles under the stationary irradiation was also investigated. Since

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MA has a dissociable proton except a thiol proton and TG does not have any dissociable proton, these were chosen as capping agents for comparison.

2. Experimental

2.1. Preparation of aqueous colloidal solutions containing CdS particles with the surface modified by capping agents

An aqueous colloidal solution of MA-CdS was prepared by referring to the method reported by Zhang et al. [16] as follows. Twenty-five milliliters of 0.02 M cadmium chloride and 25 ml of 0.03 M sodium mercaptoacetate were mixed in a 200 ml Erlenmeyer flask in a cool stirrer (FDC-900, FINE) maintained at 25 °C and then 4 ml of 0.1 M sodium hydroxide was added into it. While stirring the solution, 25 ml of 0.021 M sodium sulfide was added dropwise to the flask with a buret. The yellow-tinged, transparent colloidal solution containing MA-CdS particles was obtained. After stirring the colloidal solution for 1 h, it was allowed to stand in a refrigerator until use. The colloidal solution was used for measurements after returning to room temperature and their pH adjusted. An aqueous colloidal solution of TG-CdS was prepared by dispersing TG-CdS particles, which were synthesized by pyrolysis of thiourea in the presence of cadmium acetate and thioglycerol, into water [24,28].

The size of CdS core of both capped CdS particles was ca. 2.5 nm. It was estimated from the absorption spectra of their aqueous colloidal solutions shown in Fig. 1 by use of the relationship between the particle size and the absorption edge for CdS [29]. The pH of colloidal solutions was adjusted using sodium hydroxide or hydrochloric acid by monitoring their pH with a pH meter.

2.2. Measurements of subpicosecond transient absorption spectra

The time-resolved transient absorption spectra were measured by a pump–probe technique with a subpicosecond spectroscopy system [25,26]. The pump pulse was a 396 nm pulse generated by frequency doubling of the fundamental output ($\lambda_{max} = 792$ nm) from a Ti:sapphire regenerative amplifier using a BBO crystal and the probe pulse was a white light continuum generated by focusing the residual of the fundamental output into a 10 mm quartz cell containing water. The pulse width of both pulses, estimated by their cross-correlation using the generation of the sum frequency, was less than 1 ps. The pump pulse intensity was usually 150 μJ per pulse. The transient absorption spectra were acquired as follows. At each delay time, 10 shots of signals were accumulated and the calculation of ΔA (A: absorbance) was carried out by using them. By repeating similar acquisition and calculation, 5–12 sets of ΔA were obtained at each delay time. The average values of them were used as ΔA at each delay time for subsequent data processing. The correction of the chirp for the probe pulse was performed for the spectra by utilizing the rise time for the transient absorption of perylene in acetone.

In the measurements, the concentration of all colloidal solutions was adjusted as their absorbance at 396 nm (pumping wavelength) to be 0.6 with a 2 mm cell. The colloidal solutions were usually circulated between a non-fluorescent quartz cell (2 mm in pass length) and a sample reservoir by a roller pump during the measurements to avoid the damage from the pump pulse though ordinary quartz cells (2 mm in pass length) were also used for some of the measurements. Other details for the measurements of the transient absorption and data processing were described elsewhere [25–27].

2.3. Stationary irradiation experiments

In the stationary irradiation experiments for comparing the photo-stability of the CdS colloidal solutions, a 396 nm monochromatic light obtained by passing the light from a xenon lamp (500 W, UI-501C, Ushio Denki) through a monochromator (CT-10, Japan Spectro) was used as a light source. The concentration of all colloidal solutions was adjusted so that their absorbance at 396 nm (pumping wavelength) was 1.8 with a 10 mm cell. The experiments were usually carried out as follows. A 3 ml of each colloidal solution was transferred into a square quartz cell (10 mm path length) with a glass stopper using a transfer pipet. The colloidal solution in the cell was irradiated with a 396 nm monochromatic light for at most 4 h while stirring with a magnetic stirrer. The irradiation was interrupted and its absorption spectrum was measured every 30 min. The photo-stability of the colloidal solutions was confirmed by monitoring the change of their absorbance at 396 nm. The relative change of absorbance that reflects the dissociation and the aggregation of CdS particles was used for the discussion of the photo-stability of the CdS colloidal solutions. Other experimental details were described elsewhere [30].

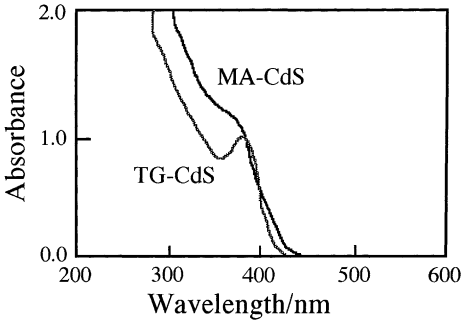

Fig. 1. Absorption spectra of the aqueous colloidal solutions containing TG-CdS and MA-CdS particles. The quartz cells with 2 mm path length were used for the measurement.

3. Results and discussion

3.1. The pH dependence of the transient absorption of aqueous colloidal solutions containing the surface-modified CdS particles

The transient absorption spectrum of an aqueous colloidal solution containing MA-CdS particles, which was measured at 2 ps after laser excitation and corrected for the chirp of a probe pulse, is shown in Fig. 2. The transient absorption spectrum of MA-CdS colloidal solution grew within the duration of a pump pulse (ca. <1 ps) over whole monitoring wavelength region as shown in the inset as an example and showed a very broad spectral shape with its absorption maximum around 700 nm, as well as that of TG-CdS colloidal solution already reported [26,27]. And further its spectral shape hardly changed, even if pH of the colloidal solution was changed. A broad transient absorption spectrum of TG-CdS colloidal solution which spreads to the whole visible wavelength region was already attributed to the overlap of three absorptions which originate from trapped electrons, trapped holes and hydrated electrons from analogy to that of ordinary CdS particles [26]. From the similarity between the transient absorptions of both aqueous colloidal solutions, it seems that the transient absorption of MA-CdS colloidal solution, measured immediately after the laser pulse excitation, also consists of the overlap of three absorptions originating from the trapped electrons, the trapped holes and the hydrated electrons. It is known that the hydrated electron production via a one-photon process such as the ejection of electrons in conduction band generated by photo-excitation is energetically impossible, and that it occurs via two-photon process like an Auger process for CdS particles in water [15,17].

The pH dependence of the transient absorption intensity (ΔA at 700 nm) of both TG-CdS and MA-CdS colloidal solutions, which was measured at 2 ps and 1 ns after laser excitation, is shown in Fig. 3. The value of Δabsorbance (ΔA) in the figure is shown as the normalized value that is the ratio of ΔA at each pH to the maximum value for each colloidal solution. As seen from the figure, the pH dependence of ΔA was not observed for TG-CdS at both delay times in the whole pH range, but it was observed for MA-CdS in lower pH range (below about 7) though the change in ΔA was moderate. Namely, ΔA for MA-CdS tends to decrease with decreasing pH in the lower pH range though the pH dependence is hardly observed in higher pH range. The similar tendency was also observed in the whole wavelength region (550–700 nm).

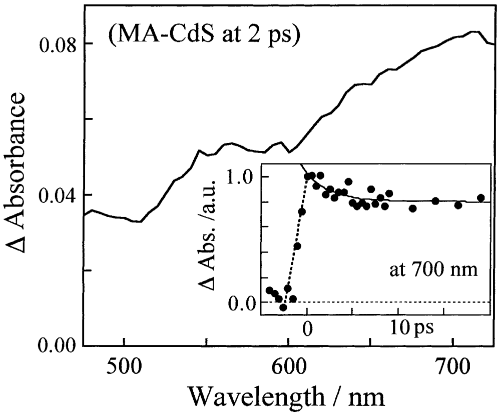

Fig. 2. The transient absorption spectrum of an aqueous colloidal solution containing MA-CdS particles, which was observed at 2 ps after laser excitation and corrected for the time dispersion (chirp) of the probe pulse. Inset is the time profile of the transient absorption at 700 nm in the early decay stage.

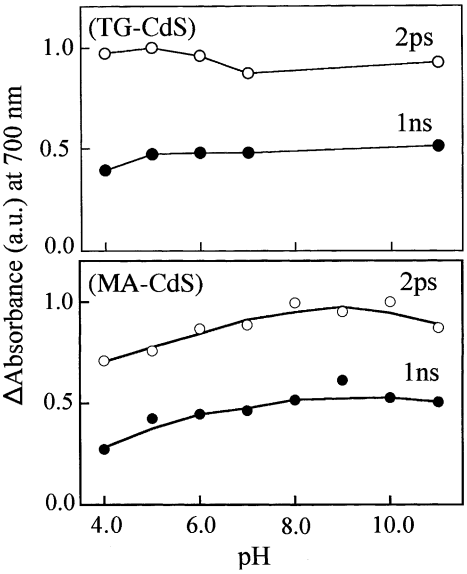

Fig. 3. The pH dependence of the intensity of the transient absorption (at 700 nm) of the aqueous colloidal solutions containing TG-CdS and MA-CdS particles, which were measured at 2 ps and 1 ns after the laser excitation.

In an aqueous colloidal solution of TiO_2, it is known that the decay of its transient absorption tends to slow down with increasing pH, since OH^- ion acts as a hole scavenger [6]. If OH^- ion similarly acts as a hole scavenger in the surface-modified CdS colloidal solution as well as in the TiO_2 colloidal solution, some portion of the hole generated by the photo-excitation of TG-CdS will be trapped by the OH^- ion in high pH range. Consequently, the hole expected to recombine with the photo-generated electrons decreases and the transient absorption intensity (ΔA) observed immediately after the laser excitation should increase with increasing pH in the longer wavelength region, where the absorption is attributed to the photo-generated electrons. However, such pH dependence was not observed, as seen from Fig. 3. In addition, the pH dependence was observed only in low pH region even for an aqueous colloidal solution of MA-CdS showing the pH effect. These results seem to indicate that OH^- ion is difficult to approach to the CdS core of the surface-modified CdS particles because of the presence of the capping agent (TG and MA) which covers the surface of the particles. Therefore, OH^- ion does not act as a hole scavenger in aqueous colloidal solutions containing surface-modified CdS particles. From such fact, it is supposed that the increase of the concentration of OH^- ion as a hole scavenger is not an appropriate reason why the transient absorption intensity (ΔA) of MA-CdS colloidal solution increases with increasing pH in the pH range of 4–7.

On the other hand, when TG and MA were compared, proton dissociation equilibrium of the carboxyl group in MA is considered as a cause of the pH dependence of the transient absorption of MA-CdS colloidal solution. The number of MA with negative charge increases in the case of MA-CdS by increasing pH, because MA combines with the CdS surface by the thiol group and the carboxyl group is free for proton dissociation. The increase of MA with carboxyl anion on the CdS surface by increasing pH is supposed to act advantageously to some extent for the hole-trapping process by capping agents, causing the increase of the trapped and hydrated electrons which escaped the recombination with holes. Though actual pK_a value of carboxyl group in the mercaptoacetic acid combining with CdS particles is uncertain, probably the value seems to fall in the region of 3–5, by considering values of free mercaptoacetic acid ($pK_a = 3.33$ [31]) and similar compounds such as acetic acid ($pK_a = 4.75$ [31]) and glycolic acid ($pK_a = 3.83$ [31]). The predicted pK_a value is different to some degree from the pH range where the pH effect appeared in the transient absorption of MA-CdS colloidal solution (Fig. 3). However, the appearance of such difference and the gradual change of ΔA in the lower pH range in Fig. 3, which are different from the prediction from the proton-dissociation equilibrium of MA, may not be strange, if a small change in the ratio between protonated and deprotonated MA does not have a sufficient effect for hole trapping ability of the particle because a large number of capping agents (MA) exist on the surface of one particle.

3.2. *The pH dependence of the photo-stability of aqueous colloidal solutions containing the surface-modified CdS particles under the stationary irradiation*

It is confirmed that the dissolution of the CdS particle occurs, when the aqueous colloidal solution of CdS is photo-irradiated under the existence of the dissolved oxygen. The reaction mechanisms are as follows, and the sulfate ion is formed [10,30].

$$CdS + h\nu \rightarrow CdS\,(e^- + h^+) \quad (1)$$

$$e^- + O_2 \rightarrow {O_2}^- \quad (2)$$

$$h^+ + CdS \rightarrow Cd^{2+}S^- \quad (3)$$

$$Cd^{2+}S^- + O_2 + {O_2}^- \rightarrow Cd^{2+} + {SO_4}^{2-} \quad (4)$$

As a whole,

$$CdS + 2O_2 \rightarrow Cd^{2+} + {SO_4}^{2-} \quad (5)$$

On the other hand, for aqueous colloidal solutions containing the surface-modified CdS particles such as MA-CdS and TG-CdS, we have already reported their photo-stability as follows [30]. The capping agent that covers the surface of CdS particles can sufficiently compete with CdS itself (Eq. (3)) for the hole trapping. Therefore, when the surface-modified CdS aqueous colloidal solutions are photo-irradiated, the increase in absorbance in their absorption band is observed with increasing irradiation time at earlier stage of the irradiation. The aggregation of CdS particles due to the oxidative elimination of capping agents from their surface, which apparently increases the absorption of the colloidal solutions by scattering an analyzing light of a spectrophotometer at absorption measurements, is more dominant than the dissolution of the particle. In this section, the pH dependence of the photo-stability (photo-aggregation and photo-dissolution) under the stationary photo-irradiation of these CdS aqueous colloidal solutions is also discussed in order to follow up the discussion on the influence of proton-dissociation equilibrium of capping agents on the hole-trapping process based on the subpicosecond spectroscopy in the previous section.

Fig. 4 shows the relationship between the absorbances at 396 nm and irradiation times for TG-CdS and MA-CdS colloidal solutions at various pH values. The absorbances in the figure are shown as the normalized value that is the ratio of absorbances at each time to that at time zero for the colloidal solutions. The data were plotted only for irradiation times in which the precipitate of particles was not observed visually. And further, the lack of plot points at some pH values for TG-CdS is due to the fact that stable colloidal solutions are not available because of the aggregation of particles. For

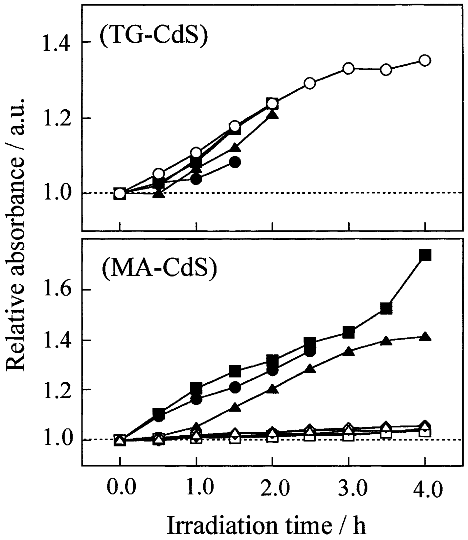

Fig. 4. Relationships between the change of absorbance at 396 nm and the irradiation time for both aqueous colloidal solutions of TG-CdS and MA-CdS at various pH values. The pH of the solutions were 4.0 (●), 5.0 (■), 6.0 (◆), 7.0 (▲), 8.0 (△), 9.0 (□), 10.0 (◇), and 11.0 (○), respectively.

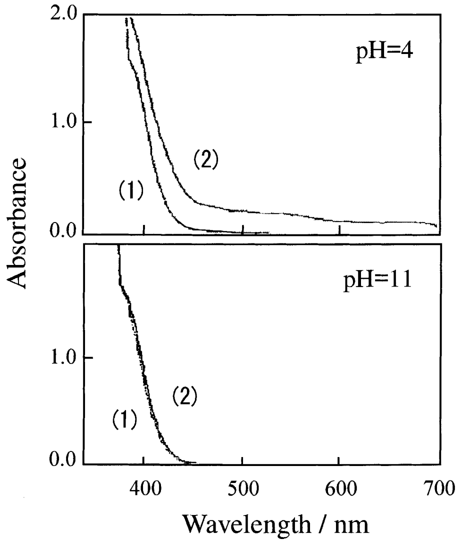

Fig. 5. Absorption spectra of an aqueous MA-CdS colloidal solution at pH = 4 and 11, which were recorded before (1) and after (2) the 396 nm irradiation for 4 h.

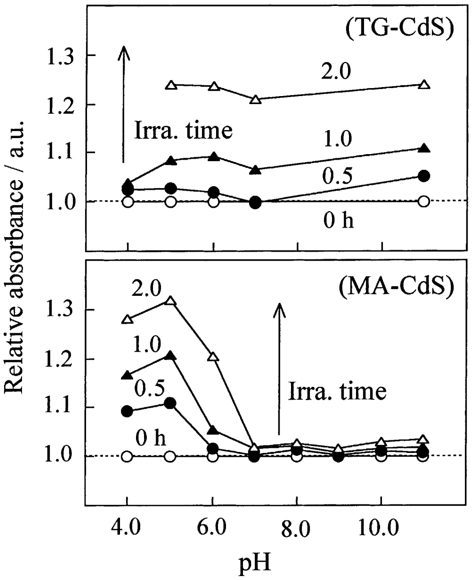

Fig. 6. Relationships between the change of absorbance at 396 nm and pH of the colloidal solutions of TG-CdS and MA-CdS at various irradiation times.

TG-CdS, the pH dependence of the absorbance at each irradiation time was considerably small though the absorbance increased with increasing the irradiation time in whole pH range measured. On the other hand, for MA-CdS, the increase of the absorbance by increasing the irradiation time was not observed in the pH range higher than pH 7. In the pH range lower than 6, however, the absorbance increased with increasing irradiation time, and further the extent of the increase clearly depended on pH of the solution. For example, absorption spectra of MA-CdS colloidal solutions at pH 4 and 11 recorded before and after the photo-irradiation for 4 h are shown in Fig. 5. It is clear that absorption spectrum of the MA-CdS colloidal solution at pH 11 hardly changes though that of the solution at pH 4 considerably increases by the photo-irradiation for 4 h. In order to better understand the pH dependence, the relationships between the normalized absorbance at 396 nm and pH of the colloidal solutions for each irradiation times are plotted in Fig. 6. As can be seen from the figure, very clear pH dependence appears at each irradiation time in the pH range lower than 7 for MA-CdS. It is very different from the case of TG-CdS in which such pH dependence of absorbance was not observed at any irradiation times, though the absorbance increased monotonously with increasing the irradiation time in whole pH range.

We discuss the cause of the difference in the pH dependence of the photo-stability under the stationary irradiation between MA-CdS and TG-CdS aqueous colloidal solutions. If the electron scavenging action of H^+ ion or the hole scavenging action of OH^- ion in the solutions influences the photo-stability of the colloidal solutions, the similar pH dependence of the photo-stability should be observed for both colloidal solutions. However, the pH dependence of the photo-stability was observed only for MA-CdS in the pH range lower than 7, but it was not observed in higher pH range for MA-CdS and in the whole pH range for TG-CdS. Therefore, this result means that H^+ and OH^- ions in the colloidal solutions do not influence the photo-stability of both colloidal solutions directly. The pH range where the pH effect appears on the photo-stability of MA-CdS was roughly the same as that where the pH dependence was observed for the subpicosecond spectroscopy described in the previous section. As already described in the previous section, the carboxyl group of MA is protonated in the lower pH range though it is in deprotonated form in the higher pH range. It seems that the hole scavenging ability of the protonated MA is lower than that of the deprotonated one. The speculation is supported from the results of subpicosecond spectroscopic study (Fig. 3). However, it seems that the elimination of the protonated MA from the particle occurs easily after trapping a hole, compared with that of deprotonated MA whose deprotonated carboxyl group acts as the hole trapping site. Consequently the aggregation of the particles occurs in the lower pH range for MA-CdS as well as the case of TG-CdS in the whole pH range. As described above, it is considered that the increase of absorbance reflects the aggregation of colloidal particles due to oxidative elimination of a capping agent from the surface of the particles. And further the aggregation for MA-CdS may be also influenced by the decrease in the surface charge due to hole trapping in neutral pH range where the protonation of carboxyl group in MA starts. Therefore, from the fact that the increase in the absorbance of TG-CdS was observed but its pH dependence was not observed by the photo-irradiation in the whole pH range, it is suggested that TG-CdS particles without dissociable protons aggregate relatively easily by photo-irradiation and the degree of the aggregation is almost same in the whole pH range.

As the reason for relatively high photo-stability of MA-CdS colloidal solution in higher pH range, it is considered that MA on the surface of the particles has almost deprotonated and the deprotonated MA does not eliminate from the particles by hole trapping or even if the elimination occurs, the aggregation of the particles is depressed due to the electrostatic repulsion among a large number of capping agents (MA) with negative charge which exist on the particle surface. However, in the lower pH range where the ratio of the deprotonated MA begins to decrease, it seems that the aggregation begins to occur due to the decrease of the surface charge and/or the elimination of MA from the particles by hole trapping.

These pH dependences for both colloidal solutions are basically similar to those obtained from subpicosecond spectroscopic experiments in which the pH dependence exists only for MA-CdS in the lower pH range as mentioned in the previous section. However, the pH dependence for the aggregation is very clear and sensitive, compared with that for the transient absorption. The difference may be interpreted as follows: when pH of the colloidal solution is lowered into the pH range where the stability of the colloidal particles is barely kept by the repulsion of their negative surface charge, the aggregation of the particles begins to occur first by a slight decrease in the surface charge of the particles due to hole trapping and/or by the oxidative elimination of a small number of MA. However, the transient absorption that reflects the total hole trapping ability of the capping agents on the particles is not so sensitive and decreases moderately because much larger number of MA compared to the photo-generated holes exists on the particle.

In conclusion, the pH dependence of transient absorption due to photo-generated electrons (trapped and hydrated electrons) in the colloidal solutions of TG-CdS and MA-CdS is similar to that of their photo-stabilities under the stationary irradiation, respectively. In the case of MA-CdS, pH of the solution influences the intensity of the transient absorption due to the photo-generated electrons and its photo-stability under the stationary irradiation in the pH range where the negative charge of carboxyl group of MA is neutralized by addition of proton in the lower pH region. Namely, the absorption intensity (ΔA) decreases and the photo-stability drops with lowering pH of the solutions for MA-CdS. However, absorption intensity and photo-stability of TG-CdS are hardly influenced by pH of the solutions. These results suggest that the negative charge of the capping agents acts advantageously on the hole-trapping process in the primary photo-chemical events of the surface-modified CdS particles and their photo-stability.

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